A Rapid Determination of Potassium with Hexanitrodiphenylamine (Dipicrylamine) Reagent.

By Hideo SUEDA and Motomi KANEKO.

(Received March 6, 1941.)

During the past few years, the feasibility of the use of Hexanitrodiphenylamine or dipicrylamine as a reagent in the quantitative determination of potassium has been reported from several sources. Most of the reports give procedures for the gravimetric method, in which the potassium is precipitated and weighed as the potassium salt of dipicrylamine, expressed as H_K. The drying at a certain temperature, cooling in a dessicator and weighing of the H_K are all quite time consuming. Colorimetric methods such as those of Kielland[1] and of Kolthoff and Bendix[2] are particularly suitable for the determination of microquantities of potassium, and a potentiometric titration method is reported by T. Kiba[3], but these methods require elaborate apparatus and are not particularly suited for rapid, simple application.

Perhaps the quickest, simplest, and in general the most satisfactory method is the direct titration of the H_K with standard acid. Kolthoff and Bendix give an acidimetric method, in which the potassium salt, H_K, (after being precipitated and washed as for the gravimetric method) is dissolved in acetone, converted to the amine with a measured excess of standard acid, and after evaporating off the acetone and then removing the precipitated amine by filtering through a glass filter, the excess acid is back titrated with standard sodium hydroxide using bromothymol blue as indicator.

After studying the above methods, the authors found that when acid is added to the acetone solution of the H_K, the reddish solution becomes yellow with the precipitation of the amine. On measuring the volume of acid added until the disappearance of the reddish color, it was found that the titration was quantitative. The addition of an excess amount of the acid followed by the back titration with sodium hydroxide until the permanent appearance of the reddish color of the H_K did not affect the accuracy of the titration. Working with sample solutions of KCl containing approximately 20 mg. of potassium, the results for a series of twelve determinations checked satisfactorily as shown in Table I. The KCl solution was calculated to be 0.252% in K_2O, and the relative errors ranged from −1.98% to +1.19%, corresponding to an average of 0.87%.

Experimental Materials: Magnesium Dipicrylaminate, H_{Mg}. A 3% solution H_{Mg} was prepared by dissolving 12 g. of dipicrylamine with 5 g. of MgO in 400 c.c. of distilled water. After stirring the solution well, it

(1) Kielland, *Ber.*, **71 B** (1938), 220.
(2) Kolthoff and Bendix, *Ind. Eng. Chem.*, Anal. Ed., **11** (1939), 94.
(3) T. Kiba, *J. Chem. Soc. Japan*, **60** (1939), 1073.

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Table 1. Titration of H_K with N/10 H_2SO_4.

Sample No.	0.1102 N H_2SO_4 (c.c.)	0.09378 N NaOH (c.c.)	Corrected Vol. H_2SO_4 (c.c.)	K_2O % Present	K_2O % Found	Relative Error (%)
1	6.85	2.54	4.79	0.252	0.250	−0.79
2	8.75	4.60	4.84	,,	0.252	0.00
3	5.68	0.95	4.87	,,	0.253	+0.40
4	5.55	0.96	4.73	,,	0.247	−1.98
5	5.85	1.20	4.83	,,	0.251	−0.40
6	5.70	1.00	4.85	,,	0.253	+0.40
7	7.50	3.10	4.86	,,	0.254	+0.79
8	6.10	1.60	4.74	,,	0.247	−1.98
9	5.53	0.92	4.77	,,	0.249	−1.19
10	8.00	3.70	4.85	,,	0.253	+0.40
11	6.00	1.40	4.81	,,	0.250	−0.79
12	6.60	2.00	4.90	,,	0.255	+1.19

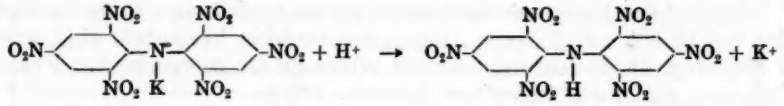
was allowed to stand overnight and was then filtered through a No. 1 G 4 glass filter.

Washing Solution A. Distilled water was cooled to 0°C. in a 100 c.c. wash bottle placed in an ice bath.

Washing Solution B. A solution of potassium dipicrylaminate saturated at 0°C. was prepared by dissolving an excess of the H_K (about 0.5 g. per 500 c.c.) in distilled water and then filtering the solution after cooling to 0°C. The solution was then kept at that temperature in a 100 c.c. wash bottle placed in an ice bath.

Standard Potassium Chloride Solution. A solution of potassium chloride was prepared by dissolving 0.9977 g. of dried KCl (Takeda, "zur Analyse") in 250 c.c. of distilled water. This solution was calculated to be 0.252% in K_2O and to contain 20.65 mg. of potassium per 10 c.c.

Experimental Procedure. 10 c.c. of the standard KCl solution were pipetted into a 100 c.c. beaker. With constant stirring, 10 c.c. of the H_{Mg} solution, corresponding to an excess of 20%, were added dropwise to precipitate the potassium as H_K. After cooling for about 15 minutes over an ice bath, the precipitate was filtered with a No. 1 G 4 glass filter, washed with about 1 c.c. of washing solution A, then with 3 or 4 c.c. of washing solution B and finally with about 1/2 c.c. of washing solution A. The H_K was then dissolved with a minimum of acetone. If more than 5 c.c. of the latter are required, the excess must be evaporated off, because it prevents a sharp color change at the titration end point. Before each titration, the acetone solution was diluted to about 15 or 20 c.c. with distilled water. It was found that the color change of from yellow to red was shaper than that of from red to yellow, so as shown in Table I, a slight excess of acid was added, and the latter was then back titrated with standard sodium hydroxide. The reaction of the H_K conversion to the amine is as follows:



Conclusion. By revising the methods reported by Kolthoff and Bendix and by T. Kiba, a simple, rapid determination of potassium with Hexanitrodiphenlyamine as the reagent was found. The potassium, after being precipitated as the potassium salt of dipicrylamine, is dissolved in acetone, and the resulting solution is directly titrated with standard acid. By taking advantage of the color change of the solution from the red of the potassium salt to the yellow of the precipitated amine, no indicator is necessary in the titration. The relative errors ranged from −1.98 to +1.19%, and the average for a series of twelve determinations was 0.87%. However, it is believed that the simplicity and rapidity of the method justify its application in routine analyses, where the accuracy of more sensitive methods may be sacrificed.

Acknowledgment is hereby made to the head of the Oi Research Laboratory of the privilege of performing the above experiments and of the permission to present this report.

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Über die unregelmässige Reihe der kolloiden Lösungen durch Elektrolyten. III-Mitteilung: Untersuchung an HgS-Solen aus verschiedenen Ausgangsmaterialien.[1]

Von **Naoyasu SATA** und **Koziro MÔRI.**

(Eingegangen am 22. März 1941.)

(1) Einleitung. Zur Untersuchung unregelmässiger Koagulationsreihe von HgS-Sol haben wir zuerst, wie gewöhnlich, das Sol nach Winssinger benutzt, welches aus $HgCl_2$ und H_2S hergestellt wird[2]. Dadurch wurde erklärt, dass diese Erscheinung stark abhängig ist, nicht nur nach den Herstellungsbedingungen des Sols, sondern auch nach kleiner Menge beigemischter Fremdsubstanzen. So ist z.B. in obengenanntem Fall bestätigt, dass Cl-Ionen des $HgCl_2$ eine wichtige Rolle spielen.

(1) N. Sata u. Y. Niwase, *Kolloid-Z*, **84** (1938), 314: N. Sata u. S. Itô, dieses Bulletin, **15** (1940), 271.

(2) C. Winssinger, *Bull. Acad. roy. Belgique*, Cl. Sci. (3), **15** (1888), 390: *Bull. Soc. Chim. France*, (2), **49** (1888), 452; H. Freundlich u. K. Schucht, *Z. physik. Chem.*, **85** (1913), 647: Das Sol ist dadurch gekennzeichnet, dass das HgS aus $HgCl_2$-Lösung mit H_2S gefällt, ausgewaschen und durch wiederholtes H_2S-Durchleiten peptisiert wird.

Nachstehend haben wir untersucht die unregelmässige Reihe an HgS-Solen welche aus versciedenen Ausgangsmaterialien hergestellt sind, unter der Meinung, die Bedeutung oder die Wirkung der beigemischten Fremdsubstanzen auf unregelmässigen Reihe zu klären.

(2) Versuch an HgS-Sol aus $Hg(CN)_2$. Prinzipiel ist die Darstellungsmethode nach Winssinger nicht anders als eine Peptisation eines chemisch niedergeschlagenes Sulfides durch wiedermaliges H_2S-Durchleiten.

Das $HgCl_2$ ist dabei als Ausgangsmaterial ausgewählt, weil es leicht erhältlich und verhältnismässig leicht löslich ist. Aus allen Hg-Salzen sollte das HgS-Sol in gleicher Weise erhalten werden können, wenn das Salz so löslich ist, dass man daraus das HgS chemisch niederschlagen könnte. Von Hg-Salzen hat das $Hg(CN)_2$ die grösste Löslichkeit, an welchem wir demnächst Untersuchung angestellt haben.

A. Lottermoser[3] hat schon das HgS-Sol aus $Hg(CN)_2$ dargestellt, indem er in $Hg(CN)_2$-Lösung den H_2S, in der Wärme unter vermindertem Druck, durchleitete. Die Reaktion verläuft nach der Gleichung:

$$Hg(CN)_2 + H_2S = HgS + 2HCN.$$

Das Nebenprodukt ist der gasförmige Cyanwasserstoff, der grösstenteils während der Reaktion mit überschüssigem H_2S ausgetrieben wird. Nun aus 2%-iger $Hg(CN)_2$-Lösung haben wir nach dieser Methode das Sol hergestellt. Überschüssiger H_2S und HCN wurde durch 30-minutiges H_2-Durchleiten ausgetrieben. Das Sol ist schwarz ganz undurchsichtig, riecht vollkommen nicht nach H_2S und sehr beständig. Der Koagulationsversuch an diesem Sol, mit $AgNO_3$ als Elektrolyt, wurde wie gewöhnlich vorgeführt. Wie aus Abb. 1 und 2 zu ersehen sind, ergeben die Koagulationskurven ausgesprochene unregelmässige Reihe. Zur Kontrolle haben wir den gleichen Versuch ausgeführt mit $Hg(CN)_2$, welches durch Umkristallisieren aus Wasser bzw. Äthylalkohol gereinigt ist. Die Resultate, welche in Abb. 3–7 ersichtlich sind, zeigen fast keinen Unterschied wie vorhergehender Versuche. (Abb. 1–2).

Inzwischen haben wir erfahren, dass das käufliche $Hg(CN)_2$ nach folgender Reaktion hergestellt worden ist.

$$HgCl_2 + 2NaOH = HgO + 2NaCl + H_2O$$

$$HgO + 2HCN = Hg(CN)_2 + H_2O$$

Also das $Hg(CN)_2$ hat auch das $HgCl_2$ als Ausgangsmaterial. Dann kann man nicht garantieren, dass wie obenerwähnt hergestelltes $Hg(CN)_2$ absolut Cl-frei ist: denn obwohl es wiederholt auf gewöhnlichem chemischem Sinne vorsichtig gereinigt ist, könnten noch die Cl-Ionen vom $HgCl_2$ (Ausgangsmaterial) durch Adsorption und andere Ursache in $Hg(CN)_2$ zurückbleiben, welche auf der unregelmässigen Koagulation des aus diesem $Hg(CN)_2$ hergestellten HgS-Sols etwaigen Einfluss ausüben

(3) A. Lottermoser, *J. prakt. Chem.* (2), **57** (1898), 484: The Svedberg, „Herstellung kolloider Lösungen anorganischer Stoffe", S. 300, Dresden u. Leipzig (1922).

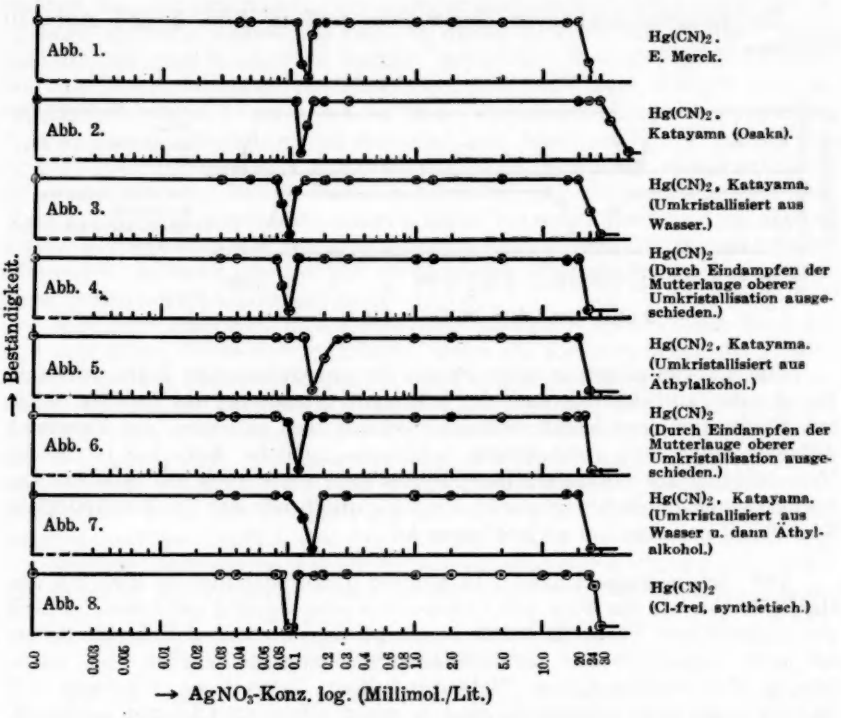
Abb. 1.
Hg(CN)2. E. Merck.
Abb. 2.
Hg(CN)2. Katayama (Osaka).
Abb. 3.
Hg(CN)2, Katayama. (Umkristallisiert aus Wasser.)
Abb. 4.
Hg(CN)2 (Durch Eindampfen der Mutterlauge oberer Umkristallisation ausgeschieden.)
Abb. 5.
Hg(CN)2, Katayama. (Umkristallisiert aus Äthylalkohol.)
Abb. 6.
Hg(CN)2 (Durch Eindampfen der Mutterlauge oberer Umkristallisation ausgeschieden.)
Abb. 7.
Hg(CN)2, Katayama. (Umkristallisiert aus Wasser u. dann Äthylalkohol.)
Abb. 8.
Hg(CN)2 (Cl-frei, synthetisch.)
Beständigkeit.
0.0 0.003 0.006 0.01 0.02 0.03 0.04 0.05 0.06 0.1 0.2 0.3 0.4 0.6 0.8 1.0 2.0 5.0 10.0 20 25 30
→ AgNO3-Konz. log. (Millimol./Lit.)

würden. Von diesem Grunde, haben wir noch einen Versuch angestellt mit absolut Cl-freiem $Hg(CN)_2$, welches folgendermassen zubereitet ist[4].

$$HgSO_4 + 2NaCN = Hg(CN)_2 + Na_2SO_4$$

Das Produkt wurde durch Umkristallisieren aus Äthylalkohol gereinigt. Die Koagulationskurve des HgS-Sols, welches aus diesem $Hg(CN)_2$ hergestellt ist, ist in Abb. 2 übergetragen. Die unregelmässige Reihe ist immer noch deutlich zu erkennen.

Jetzt ist es uns allmählich klar, dass zur unregelmässigen Reihe das Cl-Ion nicht einzige verantwortliche Fremdsubstnz ist.

(3) Versuch mit $HgSO_4$ und $Hg(NO_3)_2$. Noch gibt es $HgSO_4$ und $Hg(NO_3)_2$ als gewöhnlich käufliche Hg-Salze vor uns. Trotzdem sie beide schwer löslich sind, unter Anwendung grosser Menge gesättigter Lösungen, könnte man mit H_2S das HgS niederschlagen. Von diesem HgS haben wir in gleicher Weise das Sol hergestellt. Die Sole aus $HgSO_4$ bzw. $Hg(NO_3)_2$ sind manchmal so unbeständig, dass sie schon sich koagulieren, wenn man ihnen H_2-Gas durchleitet, um überschüssigen H_2S auszutreiben. Die Sol-Beständigkeit kann man aber sehr einfach erhöhen durch die Beschallung von Ultraschallwellen, worüber bei uns eingehend untersucht wurde[5].

(4) L. Vanino, „Präparative Chemie", Bd. I, S. 584, Stuttgart (1925).
(5) N. Sata u. Y. Niwase, *Kolloid-Z.*, **81** (1937), 294.

Die Koagulationskurven dieser Sole sind in Abb. 9 und Abb. 10 angezeigt.

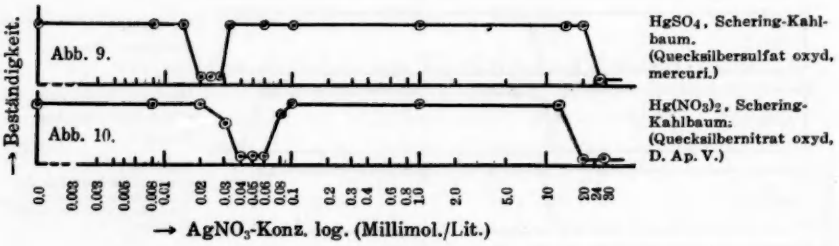
Abb. 9.
Abb. 10.
Beständigkeit.
HgSO4, Schering-Kahlbaum. (Quecksilbersulfat oxyd, mercuri.)
Hg(NO3)2, Schering-Kahlbaum. (Quecksilbernitrat oxyd, D. Ap. V.)
0.0 0.003 0.013 0.026 0.038 0.041 0.02 0.03 0.04 0.05 0.06 0.08 0.1 0.2 0.3 0.4 0.6 0.8 1.0 2.0 5.0 10 20 25 30
→ AgNO3-Konz. log. (Millimol./Lit.)

Die Kurven zeigen in allen Fällen die unregelmässige Reihe vor sich. Es ist dabei zu beachten, dass der 1-Koagulationspunkt die Tendenz zeigt, zur Stelle kleinerer Elektrolytkonzentration sich schieben, im Vergleich mit den Resultaten vorstehender Versuche. (Siehe Abb. 1–8.) Solche Verschiebung des 1-Koagulationspunktes haben wir auch mit dem Sol aus hochgereinigtem HgS[6] gemerkt, die vermutlich mit der Sol-Beständigkeit oder Sol-Konzentration zu abhängen ist.

(4) Schlussbemerkung. In voriger Untersuchung an HgS-Sol aus $HgCl_2$, haben wir die Rolle von Cl-Ionen als sehr wichtig gefunden. Durch obenausgeführte Versuche wurde bestätigt, dass die unregelmässige Reihe, bei allen HgS-Solen aus verschiedenen Ausgangsmaterialien, d.h. unabhängig der beigemischten Nebenprodukten, immer zu erkennen ist. Daraus muss man schliessen, dass es nicht allein an Cl-Ionen begrenzt, sodern alle beigemischte Fremdionen sich ähnlich verhalten würden. Wie erwähnt, vermuten wir, dass sie hauptsächlich mit der Beständigkeit bzw. Konzentration des Sols, höchstens mit der Verschiebung des 1-Koagulationspunktes zu tun haben. Die Sol-Eigenschaft die die unregelmässige Reihe zu ergeben, scheint doch immer auf HgS-Teilchen aufbehalten zu sein.

Dann könnte man es zuerst als eine einfache Umladungserscheinung durch Ionen-Adsorption verstehen. Aber die Frage, dass die unregelmässige Reihe warum nur mit bestimmten Kombinationen der Sole und Elektrolyte zu geschehen ist, wird dadurch nicht aufgelöst. Dass die Umladung der Grenzflächen, im allgemeinen, durch Adsorption hochwertiger Ionen vor sich geht, wurde schon oft, theoretisch als auch experimentell, studiert[7]. Dabei handelt es sich nur um die Ladung und Umladung reiner, neutraler Grenzfläche durch Ionen-Adsorption aus einzigem Elektrolyt. Die Sache verhält sich ganz anders und zwar sehr kompliziert, wenn die Grenzfläche anfangs nicht neutral, sondern schon Ladung trägt, worüber noch kaum untersucht worden ist[8]. Wir möchten hier darauf aufmerksam

(6) Noch unveröffentlicher Versuch von uns. Das HgS wurde gereinigt durch Kochen und Dekantieren im Quarzgefäss über 300 Tage. [Siehe auch (4)].

(7) E. A. Hauser, "Colloidal Phenomena", S. 98, New York and London (1939): "Hydrophobic Colloids", S. 58, 83. Amsterdam (1938): H. Freundlich, E. Ettisch u. P. Rona, *Z. physik. Chem.*, **116** (1925), 401.

(8) "Colloidal Phenomena", S. 107: E. J. W. Verwey, *Kolloid-Z.*, **72** (1935), 187.

machen, dass die Erscheinung der unregelmässigen Reihe gerade auf diesem Problem auffällt. Ausserdem sind von dieser Erscheinung scheinbar ganz unabhängige zwei Kategorien bekannt, namentlich die von Mastix-, Platin-Sol usw. durch hochwertigen Elektrolyt, wie $FeCl_3$ bzw. $AlCl_3$[9] und die von HgS-Sol durch einwertiges $AgNO_3$. Vorderer Fall wurde so erklärt, dass er durch Adsorption der hochwertigen Ionen, oder der von diesen Elektrolyten hydrolytisch entstandenen Kolloidteilchen zurückzuführen ist, was aber zum letzten Fall von HgS-Sol gar nicht gültig ist. Mit Mastix-Sol[1] haben wir auch schon einigen Versuche durchgeführt. Dabei wurde gezeigt, dass zur unregelmässigen Reihe nicht nur der zugefügte Elektrolyt, sondern die im Sol vorhandenen dialysierbaren Substanzen auch verantwortlich sein können.

Aus den bisherigen Untersuchungen ist es nur soweit klar, dass die unregelmässige Reihe sich stattfindet, wenn die Kolloidteilchen die Eigenschaft besitzen, sich umzuladen durch Zufügen variierender Konzentrationen geeignetes Elektrolyts. Aber welche Sorten der Kolloidteilchen, unter welchen Bedingungen diese Eigenschaft bekommen würden, bleibt fast noch unberührt. Die bekannte Regel der Umladung durch Adsorption hochwertiger Ionen hat zur Erklärung unregelmässiger Reihe keine Allgemeinheit; denn, wie erwähnt, kennen wir schon die Beispiele derselben durch einwertiges $AgNO_3$ und dreiwertiges $FeCl_3$.

Weitere Untersuchung wird fortgesetzt nach der Richtung genannten Fragestellen, die Spezifität dieser Erscheinung in erster Linie, zu klären.

Zusammenfassung.

(1) Es wurde die unregelmässige Koagulationsreihe des HgS-Sols aus verschiedenen Ausgangsmaterialien ausser $HgCl_2$ untersucht.

(2) Alle Sole, welche aus $Hg(CN)_2$, $HgSO_4$ bzw. $Hg(NO_3)_2$ als Ausgangsmaterial hergestellt sind, zeigen immer die unregelmässige Reihe vor sich.

(3) Daraus wurde konstatiert, dass zu dieser Erscheinung, im Sol beigemischte Fremdsubstanzen(-ionen) keine grosse Bedeutung hat.

(4) Es scheint, dass sie hauptsächlich die Sol-Beständigkeit, Sol-Konzentration und höchstens die kleine Formänderung der Koagulatonskurve verursacht, während die Sol-Eigenschaft die unregelmässige Reihe zu ergeben unverändert bleibt.

(5) Es wurde darauf aufmerksam gemacht, dass diese Erscheinung, aber, nicht als eine Umladungserscheinung durch Adsorption hochwertiger Ionen zu betrachten ist, weil es zwei ganz unabhängige Beispiele vorhanden sind; bei dem einen durch einwertigen, während beim anderen durch dreiwertigen Elektrolyt die unregelmässige Reihe hervorgerufen wird.

Chemisches Institut der Kaiserlichen Universität zu Osaka und Siomi-Institut für physikalische und chemische Forschung.

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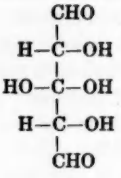
(9) H. Bechold, *Z. physik. Chem.*, **48** (1904), 418: H. Buxton u. P. Schaffer, *ibid.*, **57** (1907), 58: H. Buxton u. O. Teague, *ibid.*, **57** (1907), 72: H. Mayanagi, *Kolloid-Z.*, **39** (1926), 319.

The Formation of Polyhydroxy-dialdehydes. II.[1] *d*-Lyxo-trihydroxy-glutaric Dialdehyde and its Derivatives.

By Koichi IWADARE.

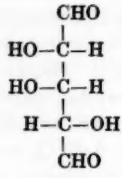
(Received April 7, 1941.)

Theoretically there should exist four dialdo-pentonoses, that is, trihydroxy-glutaric dialdehydes, and, among them, it was reported in the first paper about xylo-trihydroxy-glutaric dialdehyde (I). This communication concerns with the formation of *d*-lyxo-derivatives[2] (or *d*-arabo-derivatives) (II).



(I)

Xylo-trihydroxy-glutaric dialdehyde (described arbitrarily in chain formula)



(II)

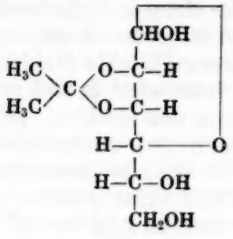
d-Lyxo-trihydroxy-glutaric dialdehyde (described arbitrarily in chain formula)

For obtaining xylo-trihydroxy-glutaric dialdehyde, 1,2-monoacetone-*d*-glucofuranose was used as the starting substance, and so monoacetone-*d*-mannose, whose constitution had not yet been ultimately determined, was analogically used for obtaining *d*-lyxo-trihydroxy-glutaric dialdehyde and was proved to be suitable for its formation. And the constitution of monoacetone-*d*-mannose was decided at the same time. This compound was first obtained as impure sirup by K. Freudenberg[3] by the partial hydrolysis of 2,3,5,6-diacetone-*d*-mannofuranose which has no substituent at 1 position. And it was identified as crystalline triacetyl-monoacetone-*d*-mannose by acetylating it with pyridine and acetic anhydride, and assumed to be 2,3-monoacetone-*d*-mannofuranose (III). It might, however, be 5,6-monoacetone-*d*-mannofuranose (IV), or, although less probable, 2,3-monoacetone-*d*-mannopyranose (V). But it was now proved to be 2,3-monoacetone-*d*-mannofuranose as supposed before. For formaldehyde was obtained by oxidizing it with lead tetracetate, and this certificated the presence of $-C(OH)-CH_2OH$ linkage. And the fact that the derivative of trihydroxy-glutaric dialdehyde was obtained by oxidizing monoacetone-*d*-mannose with lead tetraacetate was another evidence of its structure.

(1) This Bulletin, **16** (1941), 40.

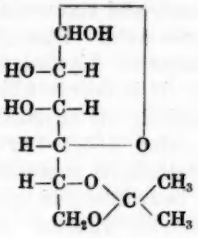
(2) The author reported briefly on these on the annual meeting of the Chemical Society of Japan in July 1940 at Sapporo.

(3) K. Freudenberg, W. Durr, and H. v. Hochstetter, *Ber.*, **61** (1928), 1740.



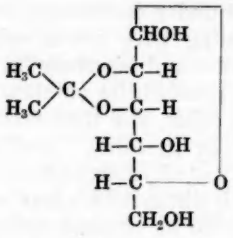
(III)

2,3-monoacetone-*d*-mannofuranose



(IV)

5,6-monoacetone-*d*-mannofuranose



(V)

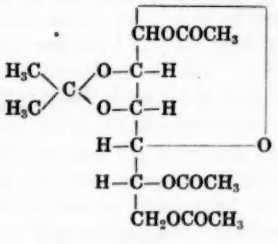
2,3-monoacetone-*d*-mannopyranose

2,3,5,6-Diacetone-*d*-mannose is dissolved in biphthalate buffer solution (*p*H 4.4), and the solution is distilled by heating in an oil bath at 140–150° for 1.5 hours, the necessary quantity of water being added during the time to keep the volume of the solution constant[3]. Then the buffer solution containing diacetone-*d*-mannose and monoacetone-*d*-mannose which is obtained by partial hydrolysis of diacetone-derivative is neutralized (phenolphthalein) and evaporated to small volume under diminished pressure, and extracted with ether for 48 hours. The ether extract is evaporated to sirup and thoroughly washed with boiling petroleum benzine to remove diacetone-mannose. The remaining sirup of monoacetone-mannose crystallizes spontaneously on standing. It is recrystallized from ether. It crystallizes in fine colourless needles. Melting point, 80.5–82° (corrected). $[\alpha]_D^{15} = +4.5°$ in water (5 minutes after solution). $[\alpha]_D^{15} = -3.7°$ (40 hours after solution). It is soluble in ether, glacial acetic acid, ethyl acetate, acetone, etc. It does not reduce Fehling's solution, or, if does, quite feebly.

Monoacetone-mannose is dissolved in glacial acetic acid, equivalent quantity of lead tetracetate is added and the mixture is warmed on a water bath at 60–65° for half an hour[4]. The evolved formaldehyde is water-distilled under diminished pressure and estimated as formaldimedon. About 70% of the theoretical quantity of formaldehyde is obtained. Thus the structure of monoacetone-*d*-mannose (III) is now established.

The crystalline 2,3-monoacetone-*d*-mannose is acetylated by pyridine and acetic anhydride in usual manner, and the same triacetyl-derivative (58.5–59°) is obtained as from sirupy one[3]. And so this derivative is ascertained to be 1,5,6-triacetyl-2,3-monoacetone-*d*-mannofuranose (VI).

2,3-Monoacetone-*d*-mannofuranose is dissolved in benzene and oxidized with lead tetraacetate. The mixture is filtered, filtrate evapo-



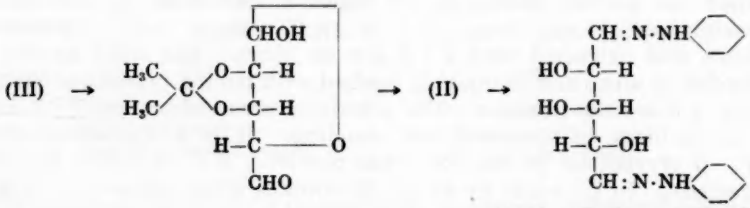
(VI)

1,5,6-triacetyl-2,3-monoacetone-*d*-mannofuranose

(4) Criegee, *Ann.*, **495** (1932), 211.

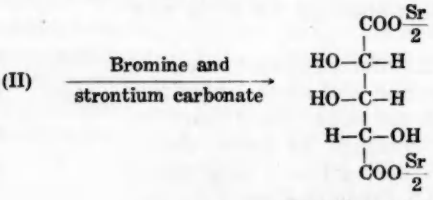
rated under diminished pressure, and the remaining sirup is hydrolized by warming with dilute sulphuric acid. Phenylhydrazine is added to the solution and *bis*-phenylhydrazone of *d*-lyxo-trihydroxy-glutaric dialdehyde soon precipitates on standing. It is recrystallized from acetone and petroleum ether, and then from alcohol. It crystallizes in fine needles. $[\alpha]_D^{15} = -72°$ in pyridine. Melting point, 168.5–169° (corrected, decomposing). *d*-Lyxo-trihydroxy-glutaric dialdehyde is obtained as sirup by decomposing its *bis*-phenylhydrazone with benzaldehyde, phenylhydrazine groups being removed as benzaldehyde-phenylhydrazone. The specific rotation of this dialdehyde is calculated by directly measuring the rotation of its water solution, which is obtained by decomposing the known quantity of its *bis*-phenylhydrazone, on the assumption that the conversion is quantitative. Thus, the specific rotatory power of *d*-lyxo-trihydroxy-glutaric dialdehyde, $[\alpha]_D^{15}$, is found to be +5°.

Bis-p-nitro-phenylhydrazone of *d*-lyxo-trihydroxy-glutaric dialdehyde is obtained by adding acidic aqueous solution of *p*-nitro-phenylhydrazine to the aqueous solution of the dialdehyde. Orange leaflets. Melting point, 207–207.5° (decomposing, corrected).



Bis-phenylhydrazone of *d*-lyxo-trihydroxy-glutaric dialdehyde (described arbitrarily in chain formula)

By oxidizing the aldehyde groups of *d*-lyxo-trihydroxy-glutaric dialdehyde with bromine, the corresponding carboxylic acid is obtained. Thus, strontium salt of *d*-lyxo-trihydroxy-glutaric acid is obtained by oxidizing the dialdehyde with bromine, generated acids being neutralized by excess of strontium carbonate.



Strontium *d*-lyxo-trihydroxy-glutarate

Experimental.

2,3-Monoacetone-d-*mannofuranose*. For preparing this substance, 2,3,5,6-diacetone-*d*-mannofuranose was first obtained by the slight modi-

fication of the usual method[5]. That is, 15 g. of *d*-mannose were mechanically shaked with 600 c.c. of acetone containing 10.5 c.c. of concentrated sulphuric acid. The greater part of *d*-mannose disappeared after half an hour, and all but coarce grains dissolved after an hour. The mixture was shaked for two hours, and then the colour of the solution was orange. It was neutralized with excess of anhydrous sodium carbonate after two hours standing, and then filtered from inorganic substances. Filtrate, now coloured in light lemon-yellow, was boiled on a water bath with a few grams of sodium carbonate and active charcoal. It was filtered after an hour, and the filtrate was concentrated first at ordinary pressure to a small volume and then evaporated to dryness under diminished pressure. The crystalline residue was recrystallized from benzine. Yield, 16 g. Ten grams of diacetone-*d*-mannose were dissolved in 250 c.c. of biphthalate buffer solution of *p*H 4.4, and the mixture was distilled in an oil bath at 140–150° for about two hours, adding water from time to time to maintain the initial volume. The distillate, received in an ice-cooled receiver, was made up to 250 c.c. with water. The acetone-content of the solution was measured by iodine-method[6], and it was found that 51% of acetone (calculated from the initial quantity of diacetone-*d*-mannose) had come to the distillate. The cooled buffer solution, which contained *d*-mannose and monoacetone- and diacetone-*d*-mannose, was neutralized to phenolphthalein, evaporated to about 25 c.c. under diminished pressure, and extracted with ether for 48 hours. The ether extract was concentrated to sirup. In order to remove diacetone-derivative completely from the sirup, 70 c.c. of petroleum benzine (70–90°) were added to it, and the mixture was heated on a boiling water bath, and stirred mechanically for one or two hours. Benzine extract was removed by decantation, and the remaining sirup was again extracted with benzine just like above-mentioned method. This procedure was repeated ten times and then the remaining sirup crystallized slowly on standing. It was recrystallized from ether. Fine colourless Needles. Melting point, 80.5–82°. (Found: C 48.64, H 7.49. Calc. for $C_9H_{16}O_6$: C 49.09, H 7.33%). $[\alpha]_D^{15}=+4.5$ in water (5 minutes after solution).→−1° (30 minutes)→−2° (one hour)→−3.7° (40 hours) (c=2.42).

*The oxidation of monoacetone-*d*-mannose.* Monoacetone-*d*-mannose (46.3 mg.) was dissolved in 3 c.c. of glacial acetic acid, 95.1 mg. of lead tetracetate were added to it, and the mixture was warmed for 30 minutes on a water bath at 60–65°. Then it was steam-distilled at 55° under reduced pressure (50 mm.), and 120 c.c., of distillate were obtained in an ice-cooled receiver. The alkaline solution of 0.5 g. of dimethylcyclohexandion-1,3 (dimedon) was added to the distillate, and the mixture was made slightly acidic by adding acetic acid. Then the colourless crystalline needles appeared at once. It was filtered after standing overnight in a refrigerator. Thus, 46.8 mg. of formal-dimedon was obtained. Melting point, 189–190° (corr.). This corresponds to 74% of the theoretical yield of formaldehyde from 2,3-monoacetone-*d*-mannofuranose.

(5) K. Freudenberg and A. Wolf, *Ber.*, **60** (1927), 232.
(6) K. Freudenberg, *Ber.*, **60** (1927), 241.

Bis-*phenylhydrazone of* d-*lyxo-trihydroxy-glutaric dialdehyde.* Mono-acetone-*d*-mannose (1.2 g.) was dissolved in 60 c.c. of benzene and lead tetracetate (2.4 g.) was added. The mixture was warmed on a water bath at 70° for ten minutes, cooled and then filtered. The precipitate was washed with acetone, and combined filtrate and washings were evaporated in vacuo to sirup, the temperature of the bath being kept below 30°. The sirup was dissolved in 50 c.c. of N/20-sulphuric acid, and warmed on a water bath for half an hour. It was warmed in vacuo to remove the isolated acetone, and phenylhydrazine (1.5 g.) was added to it. Light yellow precipitate soon appeared from the mixture. It was filtered, dried, and dissolved in acetone. Acetone solution was filtered, if necessary, and *bis*-phenylhydrazone was precipitated by adding petroleum ether. It was recrystallized from alcohol. Fine colourless needles. $[\alpha]_D^{15} = -72°$ in pyridine. Melting point, 168.5–169°. (Found: N 17.36. Calc. for $C_{17}H_{20}O_3N_4$: N 17.06%).

d-*Lyxo-trihydroxy-glutaric dialdehyde. Bis*-phenyhydrazone of *d*-lyxo-trihydroxy-glutaric dialdehyde (1 g.) was suspended in 30 c.c. of water, 1 g. of benzaldehyde added, and the mixture was mechanically stirred for an hour, heating on a water bath at 90°. After cooling, it was extracted with ether and the aqueous solution was filtered with charcoal and evaporated in vacuo to sirup. *d*-Lyxo-trihydroxy-glutaric dialdehyde thus obtained reduces Fehling's solution after several minutes at room temperature, but at once reduces it strongly when heated. The equilibrium rotatory power of *d*-lyxo-trihydroxy-glutaric dialdehyde was calculated from the rotatory power of its aqueous solution obtained by decomposition of the known quantity of its *bis*-phenylhydrazone. That is, 0.418 g. of *bis*-phenylhydrazone was suspended in 6 c.c. of water and decomposed by benzaldehyde as mentioned above. The aqueous solution was made up to 10 c.c. by adding water and its rotatory power was measured with 1 dm. tube. $\alpha_D^{15} = +0.10°$. As 0.188 g. of free dialdehyde should be obtained from 0.418 g. of its *bis*-phenylhydrazone, the specific rotatory power, $[\alpha]_D^{15}$, of *d*-lyxo-trihydroxy-glutaric dialdehyde is about +5°.

Bis-p-*nitro-phenylhydrazone of* d-*lyxo-trihydroxy-glutaric dialdehyde.* To the aqueous solution of *d*-lyxo-trihydroxy-glutaric dialdehyde, obtained as mentioned above, acidic solution of *p*-nitro-phenylhydrazine was added. Fine orange yellow precipitate soon appeared. It was filtered, and recrystallized from alcohol containing a small quantity of pyridine. Melting point, 207–207.5° (decomposing, corrected). (Found: N, 20.06. Calc. for $C_{17}H_{18}O_7N_6$ N, 20.09%).

Strontium d-*lyxo-trihydroxy-glutarate.* To the aqueous solution of *d*-lyxo-trihydroxy-glutaric dialdehyde (containing about 0.2 g. of it), 4 g. of strontium carbonate and 0.7 g. of bromine were added. The mixture was frequently shaked for several hours and then kept standing for two days. Excess bromine was removed by airing under reduced pressure, and the mixture was filtered from strontium carbonate. Then the solution was stirred on adding silver carbonate to remove bromine ion, and filtered. Sulphuretted hydrogen was passed in the filtrate to eliminate silver ion and the mixture was again filtered. The filtrate was evaporated under

reduced pressure to a small volume, and white precipitate of strontium *d*-lyxo-trihydroxy-glutarate was obtained on adding alcohol to it. (Found: Sr, 33.28. Calc. for $C_5H_6O_7Sr$: Sr, 32.98%).

1,5,6-triacetyl-2,3-monoacetone-d-*mannofuranose.* Crystalline 2,3-monoacetone-*d*-mannofuranose (0.4 g.) was dissolved in 2 c.c. of pyridine and 1 g. of acetic anhydride was added to it. The mixture was evaporated in vacuum desiccator with soda-lime and sulphuric acid, and a small quantity of dilute methyl alcohol was added to the remaining sirup, which solidified spontaneously on standing. It was recrystallized from dilute methyl alcohol. Melting point, 58.5–59°.

Summary.

(1) Monoacetone-*d*-mannose was now obtained as colourless crystalline needles and its structure was established as 2,3-monoacetone-*d*-mannofuranose (III). Melting point, 80.5–82°. $[\alpha]_D^{15}=+4.5°$ (5 minutes) → $-3.7°$ (40 hours) in water. And triacetyl-monoacetone-*d*-mannose[3] was ascertained to have the constitution (VI).

(2) *Bis*-phenylhydrazone of *d*-lyxo-trihydroxy-glutaric dialdehyde was obtained as colourless needles, starting from 2,3-monoacetone-*d*-mannofuranose. Melting point, 168.5–169°. $[\alpha]_D^{15}=-72°$ in pyridine. Equilibrium rotation of *d*-lyxo-trihydroxy-glutaric dialdehyde was measured. $[\alpha]_D^{15}=+5°$ in water. *Bis-p*-nitrophenylhydrazone of *d*-lyxo-trihydroxy-glutaric dialdehyde was obtained as orange-yellow leaflets. Melting point, 207–207.5°.

Strontium salt of *d*-lyxo-trihydroxy-glutaric acid was obtained by oxidizing the dialdehyde with bromine in presence of strontium carbonate.

In conclusion the author wishes to express his hearty thanks to Prof. B. Kubota for his kind advice for this experiment.

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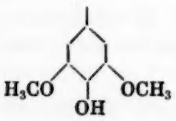
Studies on Lignin. III.[1] On the Lignin of *Paulownia imperialis*.

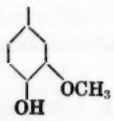
By Koichi IWADARE.

(Received April 7, 1941.)

It was recently discovered that, according to the species of woods, lignins contained in them are classified into two series.[2][3] Namely, the one contains syringyl and guaiacyl radicals as building units, while the other consists mainly of guaiacyl radicals. Among the lignins of woods which have hitherto been studied, those of birch, maple, and beech contain both syringyl and guaiacyl radicals, and those of spruce and fir contain merely guaiacyl radicals. Japanese pine and cryptomeria belong to the latters. Thus, broad-leaved trees or hard woods contain syringyl radical, while needle-leaved trees or soft woods do not. The wood of Japanese paulownia, however, is very soft, but it belongs to broad-leaved trees. So it is not clear to which series the paulownia wood belongs. This communication concerns with this point.



Syringyl-radical



Guaiacyl-radical

The lignin content of paulownia wood is measured by sulphuric acid method.[4] That is, fine saw-dust (80 mesh) of paulownia is dried at 105°, and extracted with alcohol-benzene mixture for 4 hours. Then it is added to 72% sulphuric acid to remove cellulose, hemicellulose, and other materials by hydrolysis. Water is added to the mixture to make 3% sulphuric acid solution and the solution is boiled for 4 hours and filtered. The obtained lignin is weighed and the lignin content is found to be 19.3% of dried wood. While the lignin contents of soft woods as spruce or fir are 25 to 28%, and those of hard woods as maple or birch are about 20%.

Lignin is isolated from paulownia wood by method of Harris.[5] That is, fine saw-dusts of paulownia wood, extracted first with alcohol-benzene mixture, then with alcohol, and finally with hot water, are treated with 70% sulphuric acid for 20 hours at 10°. Then the mixture is diluted with water to make 3% sulphuric acid solution, boiled, and then filtered. The methoxyl-value of the lignin thus obtained is 20.7%, and is same as that of the lignin of maple wood obtained by Harris. As the methoxyl-contents of the lignin of needle-leaved trees such as spruce, fir, or cryptomeria are

(1) K. Iwadare, *J. Chem. Soc. Japan*, **62** (1941), 186.
(2) K. Freudenberg and H. Fr. Müller, *Ber.*, **71** (1938), 1821.
(3) Hibbert et. al., *J. Am. Chem. Soc.*, **61** (1939), 509, 516, 868, 2198; **62** (1940), 986, 2149; **63** (1941), 312.
(4) C. J. Ritter, R. M. Seborg, and R. L. Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **4** (1932), 202.
(5) E. C. Sherrard and E. E. Harris, *Ind. Eng. Chem.*, **24** (1932), 103; E. E. Harris, E. C. Sherrard, and R. L. Mitchell, *J. Am. Chem. Soc.*, **56** (1934), 889; E. E. Harris, *J. Am. Chem. Soc.*, **58** (1936), 894.

15–17%, the paulownia belongs apparently to the series of so-called hard-wood lignin.

Paulownia wood is ethanolised by usual method. Dry saw-dust, the resinous materials of which have been removed as mentioned above, is heated for 48 hours with absolute alcohol containing hydrogen chloride. The experimental data are as follows. (Table 1).

Table 1.[6]

		Weight (g.)	Percentage (%)	
			Calc. for wood-meal	Calc. for lignin
Starting substance	Paulownia wood-meal dried at 100-105°	70		
	Lignin content of the wood-meal (by 72% sulphuric acid method[4])	13.5	19.3	
Reaction products	Residual wood-meal	38	54	
	Lignin content of the residual wood-meal	2.8	7.4	21
	Lignin removed by ethanolysis	10.7		79
	Ethanol lignin	2.5		18
	Materials extracted with benzene — From aqueous solution	5.5		41
	Materials extracted with benzene — From ethanol lignin	3.5		26
	Materials extracted with benzene — Total	9.0		67

The methoxyl-content of the ethanol lignin is 26.9%, calculating ethoxyl as methoxyl.

The benzene solution of the extracted materials is shaked with aqueous solutions of sodium bisulphite, sodium bicarbonate and sodium hydroxide respectively and fractionated into aldehydic, acidic, phenolic, and neutral materials. (Table 2).

Table 2.[6]

	Weight (g.)	Percentage (Calc. for total lignin) (%)
Materials extracted with benzene	9	67
Aldehydic	0.8	6
Acidic	0.2	1.5
Phenolic	3.7	27
Neutral	0.4	3
Total	5.1	37.5%

(6) Some of the percentages in table 1 and 2 should be corrected by the factor $L/(L+OC_2H_5)$ owing to the ethoxyl group added to lignin. (L is the molecular weight of the building unit of lignin.)

The aldehydic fraction is dissolved in ethyl alcohol, and saturated ethyl alcohol solution of anhydrous potassium acetate and 2% potassium hydroxide-ethyl alcohol solution are added to it. Orange-yellow needles appear within half an hour. Adding semicarbazide hydrochloride to this precipitate, colourless crystals melting at 210.5–211.5° are obtained. This melting point agrees with that of monosemicarbazone of syringoylmethylketone (210–210.5°) obtained by Hibbert from maple wood, and so this compound obtained from paulownia lignin is identified as syringoylmethylketone. It is therefore established that paulownia lignin contains syringyl radicals, and belongs to so-called hard wood lignin.

Recently, it was reported by K. Freudenberg,[7] that vanilline was obtained by oxidation of spruce wood-meal with nitrobenzene, and now paulownia wood-meal was oxidized by the same method. That is, paulownia wood-meal is heated in an autoclave at 160° with nitrobenzene and aqueous alkaline solution. From the reaction mixture nitrobenzene is removed by water-distillation. The residual solution is filtered, made slightly alkaline with sodium bicarbonate, and extracted continuously with benzene for 72 hours. Benzene extract corresponds to about 14% of the initial wood-meal and therefore to 70% of the lignin contained in it. A small portion of the benzene extract is suspended in water and acidic aqueous solution of 2,4-dinitrophenylhydrazine is added. The precipitated 2,4-dinitrophenylhydrazone is weighed, and the whole quantity of the aldehydes in the benzene extract is calculated from it. It corresponds to about 38% (by weight) of the lignin existing in the initial wood-meal, assuming the aldehydes as vanilline, and to about 43%, assuming them as syringylaldehyde.

Another portion of the benzene extract is dissolved in alcohol, filtered if necessary, and alcohol which contains dry ammonia is added. Yellow crystals appear immediately on standing. 2,4-Dinitrophenylhydrazone melting at 234.5–235° is obtained from it, so it is identified as the syringaldehyde derivative.

Experimental.

Lignin content of paulownia wood-meal. Paulownia wood-meal (80 mesh) was dried at 105°, and 1.971 g. of it were extracted with benzene-alcohol mixture in Soxlet-apparatus for 4 hours. It was filtered, washed with alcohol, and heated with 400 c.c. of water in a boiling water bath for 3 hours. It was filtered, dried and mixed with 25 c.c. of 72% sulphuric acid. After 2 hours, it was diluted with water to make 3% sulphuric acid solution and boiled for 4 hours. Insoluble lignin was weighed by filtering the solution with a tared glass-filter. Brown lignin (0.380 g.) was obtained. This corresponds to 19.3% of the initial wood-meal.

The methoxyl-value of paulownia lignin. Paulownia wood-meal (24 g.) was mixed with 240 c.c. of 70% sulphuric acid, and stirred for 3 hours at 10°. After standing overnight in a refrigerator at 10°, it was poured in 9 l. of water and boiled for 4 hours. It was filtered and air-dried.

(7) K. Freudenberg, W. Lautsch, and K. Engler, *Ber.*, **73** (1940), 167.

Yield, 5 g. The methoxyl-value of the lignin dried at 100° in vacuo over phosphorous pentoxide is 20.7%.

The ethanolysis of paulownia wood-meal. Paulownia wood-meal (70 g.), freed from resinous materials by extracting with alcohol-benzene mixture, alcohol, and then with hot water, was boiled for 48 hours with 850 c.c. of absolute ethyl alcohol containing 2% of hydrogen chloride. It was filtered, washed well with alcohol, and the combined filtrate and washings were neutralized with sodium ethylate, and evaporated under reduced pressure to 150 c.c. It was poured into 1.2 l. of water, and filtered. The precipitate was dried and extracted ten times by shaking mechanically with benzene (50 c.c.). The filtrate was evaporated to 200 c.c. and extracted continuously with benzene for 48 hours. Both benzene extracts were evaporated, and 3.5 g. and 5.5 g. of sirups were obtained respectively. The sirups were dissolved in benzene and the combined benzene solution was extracted many times with aqueous solution of sodium bisulphite, sodium bicarbonate and sodium hydroxide to fractionate it into aldehydic, acidic, phenolic and neutral materials. The sodium bisulphite extract was made acidic by sulphuric acid, isolated sulphurous acid being removed under diminished pressure, and extracted continuously with benzene. The benzene extract was evaporated to sirup (0.8 g.) and dissolved in absolute ethanol (25 c.c.). The ethyl alcoholic solution of sodium acetate was added to it, and 2% alcoholic solution of sodium hydroxide was added to the mixture to make it slightly alkaline. Orange-yellow needles precipitated within half an hour. It was filtered, and 20 mg. of the precipitate were dissolved in 1 c.c. of water, and 14 mg. of semicarbazide hydrochloride and 20 mg. of potassium acetate were added. It was filtered after 2 hours. Melting point, 210.5–211.5° (corrected). This corresponds to monosemicarbazone of syringoylmethylketone.

The methoxyl-value of ethanol lignin is 26.9%, and that of the lignin isolated from the residual wood-meal by 70% sulphuric acid method is 21.0%, which is almost equal to the methoxyl-value of the lignin from initial wood-meal. Other experimental data are given in tables 1 and 2.

The oxidation of paulownia wood-meal with nitrobenzene. Paulownia wood-meal (35 g.) was heated for five hours in an autoclave with 400 c.c. of 10% sodium hydroxide solution and 20 c.c. of nitrobenzene. The mixture was water-distilled, and remaining solution was filtered. The filtrate was made slightly acidic by adding hydrochloric acid, and then made slightly alkaline by sodium bicarbonate. It was continuously extracted with benzene for 72 hours, and the benzene solution was evaporated in vacuo. The residual sirup was 5.0 g. It was dissolved in 100 c.c. of benzene, and 1 c.c. of it was evaporated and acidic aqueous solution of 2,4-dinitrophenylhydrazine was added to it. Calculating from the weight (58.2 mg.) of 2,4-dinitrophenylhydrazone obtained, 2.66 g. or 2.92 g. of aldehydes should exist in the benzene extract, if the aldehydes are assumed to consist only of vanilline or syringaldehyde respectively. They correspond to about 38% or 43% (by weight) of the lignin existing in the initial wood-meal.

Benzene extract (0.7 g.) was dissolved in 5 c.c. of alcohol, filtered, and alcohol which contained dry ammonia was added. Yellow crystals

were obtained. It was dissolved in ethanol containing a few drops of concentrated hydrochloric acid, and 2,4-dinitrophenylhydrozine was added. Red crystals melting at 234.5–235° were obtained. This melting point agrees with that of 2,4-dinitrophenylhydrazone of syringaldehyde.

The residual aqueous solution, which had been extracted with benzene, was made acidic by adding hydrochloric acid and extracted continuously with benzene. Thus, 1.2 g. of acidic fraction were obtained.

Summary.

Although paulownia wood is very soft, its lignin belongs to so-called hard-wood lignin, and it contains both syringyl and guaiacyl radicals. These facts are established by the measurements of the lignin content and of the methoxyl value of the paulownia wood lignin, and by the ethanolysis and oxidation with nitrobenzene.

In conclusion, the author wishes to express his hearty thanks to Prof. B. Kubota for his kind advice for this experiment.

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